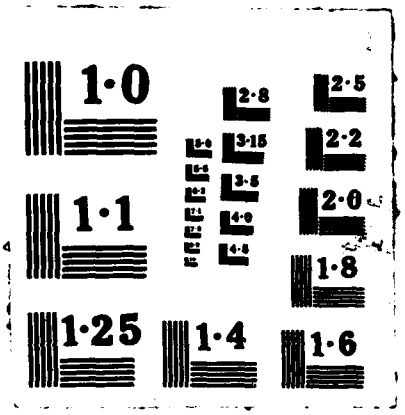
AD-A187 457 THE FIRST GALLIUM-ARSENIC COMPOUND CONTAINING A SINGLE GA3AS UNIT ISOLAT (U) DUKE UNIV DURHAM NC DEPT OF CHEMISTRY R L WELLS ET AL 28 OCT 87 N00014-83-K-0572 1/1

UNCLASSIFIED F/G 7/2 NL


1·0
1·1
1·25
1·4
1·6
2·8
3·15
3·5
4·0
2·5
2·2
2·0
1·8

DTIC FILE COPY

(12)

Unclassifie

SECURITY CLASSIFICA

AD-A187 457

ENTATION PAGE

1a. REPORT SECURI Unclassifi...	1b RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AU...	3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; distribution unlimited
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION Department of Chemistry Duke University	6b. OFFICE SYMBOL (If applicable)
6c. ADDRESS (City, State, and ZIP Code) Durham, NC 27706	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research
	7b. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217-5000
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable)
8c. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217-5000	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-83-K-0572
	10 SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO	PROJECT NO.	TASK NO	WORK UNIT ACCESSION NO
NR	053	841	

11. TITLE (Include Security Classification)
The First Gallium-Arsenic Compound Containing a Single Ga_3As Unit: Isolation and Crystal Structure of $[(thf)Br_2Ga]_3As$ (thf = tetrahydrofuran)

12 PERSONAL AUTHOR(S)
R.L. Wells, S. Shafieezad, A.T. McPhail, and C.G. Pitt

13a TYPE OF REPORT	13b TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Technical	FROM _____ TO _____	87/10/28	7

16 SUPPLEMENTARY NOTATION
Accepted for Publication in J. Chem. Soc., Chem. Commun.

17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Gallium-Arsenic, Crystal Structure

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

$[(thf)Br_2Ga]_3As$, isolated from the reaction of $(Me_3Si)_3As$ with $GaBr_3$, has been shown by X-ray crystallographic analysis to be the first example of a compound containing a single Ga_3As unit.

20 DISTRIBUTION / AVAILABILITY OF ABSTRACT	21 ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS	Unclassified

22a NAME OF RESPONSIBLE INDIVIDUAL	22b TELEPHONE (Include Area Code)	22c OFFICE SYMBOL
Richard L. Wells	(919)684-6404	

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted
All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

OFFICE OF NAVAL RESEARCH

Contract N00014-83-K-0572

R&T Code 4135008---02
Replaces Old
Task #NR053-841

Technical Report No. DU/DC/TR-07

The First Gallium-Arsenic Compound Containing a Single Ga_3As Unit: Isolation and Characterization of $[(thf)Br_2Ga]As$ (thf = tetrahydrofuran)

by

R. L. Wells, S. Shafieezad,
A. T. McPhail, and C. G. Pitt

Prepared for Publication in
J. Chem. Soc., Chem. Commun.

Duke University
Department of Chemistry
Durham, NC 27706

October 28, 1987

The First Gallium-Arsenic Compound Containing a Single Ga_3As Unit: Isolation and Crystal Structure of $[(thf)Br_2Ga]_3As$ (thf = tetrahydrofuran)

Richard L. Wells*, Soheila Shafieezad, Andrew T. McPhail, and Colin G. Pitt*

Department of Chemistry, Paul M. Gross Chemical Laboratory, Duke University, Durham, NC 27706 U.S.A.

$[(thf)Br_2Ga]_3As$, isolated from the products of the reaction of $(Me_3Si)_3As$ with $GaBr_3$, has been shown by X-ray crystallographic analysis to be the first example of a compound containing a single Ga_3As unit.

Prior to 1986, there were no published examples of gallium-arsenic compounds containing a single $AsGa_3$ or Ga_3As unit. However, during that year two compounds of the first type having three-coordinate Ga and three-coordinate As were reported, $(R_2As)_3Ga$ (R = Mes[1], Bu^t[2]). We now report the isolation and structure of a compound of the second type having, in this initial case, four-coordinate Ga and three-coordinate As, $[(thf)Br_2Ga]_3As$ (thf = tetrahydrofuran) (1). The reaction of $(Me_3Si)_3As$[3] with $GaBr_3$, which affords the $(Br_2Ga)_3As$ species found in (1), appears to be the first reported of a tri(silyl)arsine being utilized to form the Ga-As linkage, and

over

cont'd → it further demonstates the importance of silylarsines in the area of preparative gallium/arsenic chemistry[4a]. (Keywords: Gallium, Arsenic) ←

A toluene solution of $(Me_3Si)_3As$ (0.41 g, 1.39 mmol), cooled to -15 °C, was added† to a toluene solution of $GaBr_3$ (1.29 g, 4.18 mmol) at -15 °C. After 15 h at -15 °C, stirring at room temperature for 24 h, and removal of solvent and Me_3SiBr (4.18 mmol, 100% yield) under vacuum, a yellow powder was obtained. A thf solution of the powder at -15 °C afforded, after several days, $[(thf)Br_2Ga]_3As$ (1) as pale yellow crystals (0.37 g, 27% yield).‡

The structure of (1) is illustrated in Figure 1.§ The As atom lies on a crystallographic $\underline{C}_3$ axis and, with a Ga-As-Ga′ angle of 94.4(1)°, the Ga_3As skeleton is pyramidal. At Ga, the geometry is distorted from tetrahedral in response to the different steric demands of the substituents. Thus, the three smallest bond angles (mean 100.6°) all involve the thf oxygen atom while the larger of the significantly different As-Ga-Br angles [As-Ga-Br(1) 124.0(2)°, As-Ga-Br(2) 115.4(2)°] is associated with the Ga-Br bond which more nearly eclipses an As-Ga bond [dihedral angles: Br(1)-Ga-As-Ga′ 16.5°, Br(2)-Ga-As-Ga″ 63.7°]. The Ga-As bond length at 2.404(4) Å is the shortest distance yet recorded for a bond between a four-coordinate Ga and a three-coordinate As. It is significantly smaller than that of 2.437(1) Å in $\{[(Me_3SiCH_2)_2As]_2GaBr\}_2$ (previously the shortest recorded)[4b] and much less than the shortest [2.475(1) Å] of the two corresponding lengths in the cluster $[(PhAsH)(R_2Ga)(PhAs)_6(RGa)_4]$ (R = Me_3SiCH_2)[5] as well as the shortest [2.470(1) Å] of four such distances in $\{[(Me_3SiCH_2)_2As]_3Ga\}_2$.[6]

Interestingly, the Ga-As bond length in (1) is also smaller than the shortest Ga-As distance [2.470(1) Å] in $(Mes_2As)_3Ga$[1] which contains three-coordinate Ga and three-coordinate As.

Finally, it should be noted that thus far we have been unsuccessful in our attempts to isolate a monomeric compound containing a Ga_3As unit having three-coodinate Ga and As; however, it is anticipated that with the appropriate substituents on Ga this should be possible.

We thank the Office of Naval Research for financial support.

References

1 C. G. Pitt, K. T. Higa, A. T. McPhail, and R. L. Wells, Inorg. Chem., 1986, 25, 2483.

2 A. M. Arif, B. L. Benac, A. H. Cowley, R. Geerts, R. A. Jones, K. B. Kidd, J. M. Power, and S. T. Schwab, J. Chem. Soc., Chem. Commun., 1986, 1543.

3 V. G. Becker, G. Gutekunst, and H. J. Wessely, Z. anorg. allg. Chem., 1980, 462, 113.

4 (a) C. G. Pitt, A. P. Purdy, K. T. Higa, and R. L. Wells, Organometallics, 1986, 5, 1266; (b) A. P. Purdy, R. L. Wells, A. T. McPhail, and C. G. Pitt, Organometallics, in press.

5 R. L. Wells, A. P. Purdy, A. T. McPhail, and C. G. Pitt, J. Chem. Soc., Chem. Commun., 1986, 487.

6 R. L. Wells, A. P. Purdy, K. T. Higa, A. T. McPhail, J. Organomet. Chem., 1987, 325, C7.

Footnotes

† All manipulations were performed under a dry nitrogen atmosphere.

‡ Compound (1) m.p. 125-145 °C (decomp.). A satisfactory elemental analysis was obtained (C, H and Br).

§ Crystal data: $C_{12}H_{24}AsBr_6Ga_3O_3$ (1), M = 979.86, trigonal, space group $R3c$, $a = b = c$ = 11.765(1) Å, $\alpha = \beta = \gamma$ = 107.04(1)°, U = 1354.7 Å^3, Z = 2, D_c = 2.402 g cm^{-3}, μ(Cu-$K\alpha$ radiation, λ = 1.5418 Å = 154.7 cm^{-1}. Crystal dimensions: 0.20 x 0.30 x0.30 mm (sealed inside a thin-walled glass capillary). Intensity data (660 independent forms) were recorded on an Enraf-Nonius CAD-4 diffractometer (Cu-$K\alpha$ radiation, incident-beam graphite monochromator; ω-2θ scans, $\theta_{max.}$ = 55°). The crystal structure was solved by direct methods. Full-matrix least-squares refinement [375 absorption-corrected reflections with $I > 3.0\sigma(I)$] of non-hydrogen atom positional and anisotropic thermal parameters converged at R = 0.056 [R_w = 0.071, $w = 1/\sigma^2(|F_o|)$]. Atomic co-ordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Legend For Figure

Figure 1. ORTEP plot of $[(thf)Br_2Ga]_3As$ (1). Selected distances (Å) and angles (°): Ga-As 2.401(4), Ga-Br(1) 2.321(5), Ga-Br(2) 2.341(7), Ga-O(1) 1.99(2), Ga-As-Ga′ 94.4(1), As-Ga-Br(1) 124.0(2), As-Ga-Br(2) 115.4(2), As-Ga-O(1) 102.5(7), Br(1)-Ga-Br(2) 110.5(2), Br(1)-Ga-O(1) 99.2(6), Br(2)-Ga-O(1) 100.1(9).

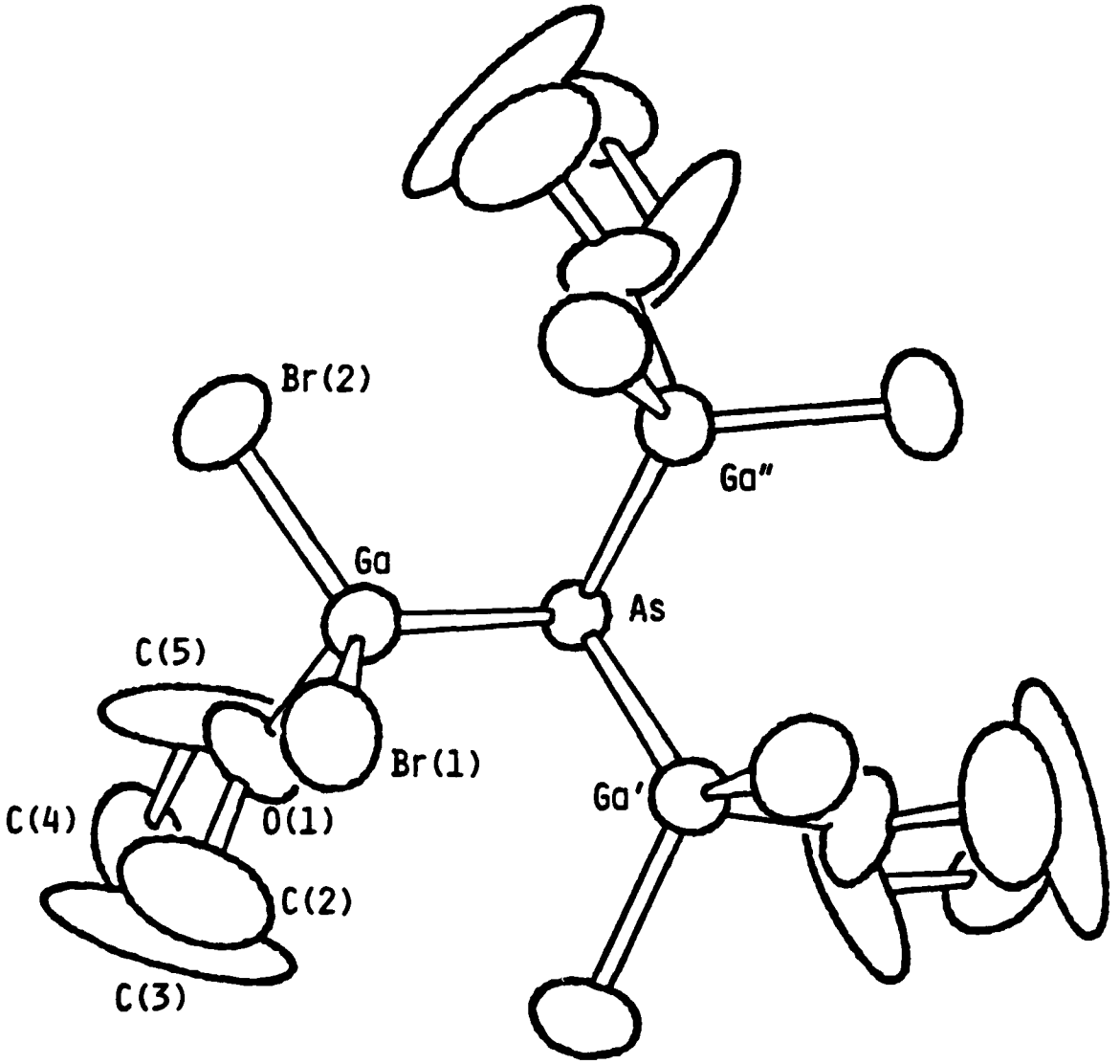


Figure 1

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1
Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1

END

FEB.

1988

DTIC